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Dynamics of Spin and Orbital Phase Transitions in YVO_3

Dmitry A. Mazurenko,* Agung A. Nugroho, Thomas T. M. Palstra, and Paul H. M. van Loosdrecht†

Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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YVO_3 exhibits a well separated sequence of orbital and spin order transitions at 200 and 116 K, followed by a combined spin-orbital reorientation at 77 K. It is shown that the spin order can be destroyed by a sufficiently strong optical pulse within less than 4 ps. In contrast, the orbital reordering transition from *C*-type to *G*-type orbital order is slower than 100 ps and goes via an intermediate nonthermal phase. We propose that the dynamics of phase transitions is subjected to symmetry relations between the associated phases.

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The dynamics of phase transitions is an important and rapidly growing area of modern science. The interest in this topic is not only limited to the condensed matter community, but also touches other areas of science ranging from geology [1] to the modeling of traffic dynamics [2]. At the same time, the exponential growth of publications in this area has also been driven by applications in optical switching [3] and phase-change data storage [4] where throughput is ultimately limited by the phase-change rate. A phase transition may be triggered by a short optical pulse and subsequent dynamics of the phase change are available for monitoring by time-resolved optical and x-ray techniques. Up to now the research has been primarily focused on single phase changes. It has been demonstrated that some optically induced phase transitions [5–13] may occur on picosecond and subpicosecond time scales, much faster than phonon-phonon or even electron-phonon equilibration times. These so-called nonthermal phase transitions occur only at excitation power densities exceeding a certain critical value P_s, which was found to be slightly higher than the power required to trigger a phase transition under equilibrium conditions P_c [5,6]. However, some other phase transitions are much slower and last a fraction of a nanosecond or longer, which is sufficient for establishing equilibrium between electrons and lattice [14,15]. This Letter demonstrates that these fast- and slow-type phase transitions may simultaneously occur in the same material if the involved phases possess certain symmetry relation. Moreover, when both transitions are triggered by the same optical pulse, a transition normally taking place at higher temperature may occur faster than a transition normally taking place at lower temperature.

The material of choice used in the present study is the perovskite YVO_3, which shows a sequence of orbital and spin transitions as a function of temperature. This material has a phase diagram similar to $LaVO_3$, for which nonthermal melting of the orbital order was recently reported [12]. An important difference is that spin and orbital order phase transition temperatures in $LaVO_3$ are so close to each other that the different phases are not distinguishable in optically induced experiments. In contrast, the transitions in YVO_3 are far apart allowing study of the multiple phase changes. At room temperature this crystal is paramagnetic and has an orthorhombic *Pbnm* structure. At $T_{OO} = 200$ K, the material undergoes a phase transition into an orbitally ordered phase, in which the d_{xz}/d_{yz} orbital occupation alternates in all three crystallographic directions (*G*-type ordering) [16,17]. This transition is accompanied by a symmetry lowering into a $P2_1/b11$ monoclinic form [18] with a continuous expansion along the *b* axis and a contraction along the *a* and *c* axes [19]. Recently, Miyasaka *et al.* [20] suggested that this phase involves short-range correlation or fluctuation of the orbital *C* type. Below another phase transition at $T_N = 116$ K the spins form an antiferromagnetic arrangement in the *ab* plane with a ferromagnetic arrangement along the *c* axis (*C*-type ordering). Finally, at $T_{CG} = 77$ K, YVO_3 undergoes a first-order phase transition, changing the spin ordering from *C* to *G* type with a simultaneous change in the orbital ordering from *G* to *C* type. Quite unusually, this phase transition is accompanied by an increase in the symmetry [21] of the lattice back to the orthorhombic *Pbnm* form [17,18,20,22,23]. All three phase transitions manifest themselves as pronounced changes in the optical absorption in three spectral bands associated with $d - d$ transitions, located at 1.8, 2.4, and 3.3 eV [18]. This allows the dynamics of the phase transitions to be traced by monitoring the optical reflectivity [18].

Time-resolved two-color pump-probe experiments were performed on *bc*-oriented polished platelets of a YVO_3 single crystal placed in a helium-flow cryostat. Details of the sample growth can be found in Ref. [18]. The optical pump and probe pulses were derived from an amplified Ti:sapphire laser with a repetition rate of 1 kHz, in combination with an optical parametric amplifier. In order to ensure quasihomogeneous excitation of the sample, the pump wavelength was set to 800 nm (1.55 eV), which is slightly below the band gap of YVO_3. For probing, a

wavelength of 630 nm (1.97 eV) was chosen, since at this wavelength the reflectivity is sensitive to all the phase transitions.

Figure 1 displays some typical time traces of the transient reflectivity for different excitation power densities at $T = 25$ K, i.e., in the C-type orbitally ordered phase. All traces show an abrupt change just after arrival of the pump pulse followed by kinetics with pronounced temporal oscillations in the transient reflectivity with a period of about 19 ps [24]. These oscillations are the result of interference of the probe light reflected from the sample surface and from the longitudinal acoustic strain wave formed by an optically induced stress and propagated with 7.2 ± 0.5 km/s. The present discussion will be focused on the nonoscillation part of the transient reflectivity dynamics, which can be quite faithfully fitted by a double-exponential decay function with $\tau_1 = 3 \pm 1$ ps and $\tau_2 = 45 \pm 10$ ps for the fast and slow decay terms, respectively.

For weak optical excitations [Fig. 1, curves a and b] the slow decay dominates the transient reflectivity dynamics; the transient reflectivity is positive over most of the experimental time scale and rises with increasing excitation power density P. However, when P is above a critical value the slow decay component suddenly disappears [Fig. 1, curves c–e]. Moreover, the saturation level of the transient reflectivity now becomes more negative as the excitation strength increases. The drastic change in the transient reflectivity dynamics at $P = P_c$ is clear in the inset of Fig. 1, which plots the amplitudes of the transient reflectivity decay components as a function of the pump power density. Upon increasing the excitation power density, the amplitude of the slow decay component (solid squares) grows linearly up to P_c, above which it rapidly decreases before vanishing at $P_s = 1.7P_c$. In contrast, the amplitude of the fast decay component (open triangles) remains quite sizable even for $P > P_s$. We found that P_c is essentially independent of the initial lattice temperature as long as $T < T_N$, but depends strongly on the excitation wavelength and varies from $P_c = 55$ mJ/cm^2 to $P_c = 3$ mJ/cm^2 for pump wavelengths of 800 and 400 nm, respectively. This is most likely due to a substantial change in the absorption, which varies by about an order of magnitude in this spectral range [18].

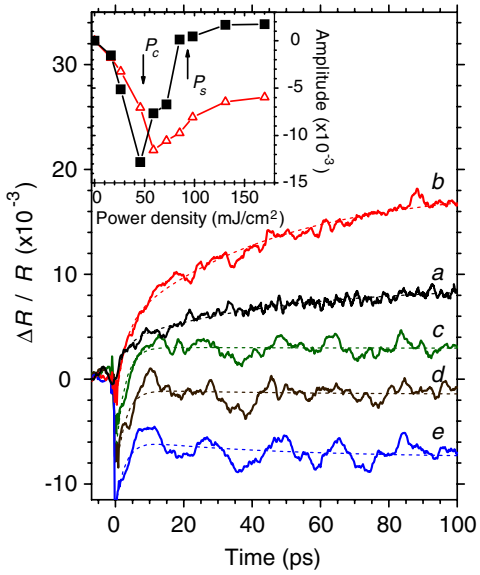

FIG. 1 (color online). Dynamics of the transient reflectivity of YVO_3 following optical excitation with a power density of (a) 25 mJ/cm^2, (b) 45 mJ/cm^2, (c) 85 mJ/cm^2, (d) 100 mJ/cm^2, and (e) 170 mJ/cm^2. Solid lines show the experimental data measured at 25 K and dotted lines represent fits of a double-exponential function to the experimental data. The inset shows the amplitude of the fast (△) and slow (■) decay components of the transient reflectivity extracted from the fits as a function of the excitation power density.

The observed threshold behavior provides direct evidence for a photoinduced phase transition, where P_c and P_s correspond to the critical power densities required for activating the slow and fast phase transition regimes, respectively. In order to assign these transitions to a specific phase change, we measured the power dependence of the transient reflectivity starting from the three different phases of YVO_3: the C-type orbital ordered phase at $T = 50$ K [Fig. 2(a)], the G-type orbital ordered phase with C-type spin order at $T = 100$ K [Fig. 2(b)], and the G-type orbital ordered phase with disordered spins at $T = 140$ K [Fig. 2(c)]. The data are presented for two specific times after excitation: at 4-ps delay, just after the fast τ_1 dynamics ends (open circles), and at 100-ps delay, when the transient dynamics is over and the reflectivity has reached a plateau (solid squares). The photoinduced phase transition manifests itself as an anomaly at P_c [Figs. 2(a) and 2(b)], which appears below T_N only. Quite importantly, the shape and the threshold of the power dependence does not change when the sample temperature crosses T_{CG}. However, when the temperature approaches T_N from below, the anomaly in the power dependence diminishes [Fig. 2(b)] and finally disappears at T_N. For $T > T_N$ the transient reflectivity has a monotonic linear dependence on the excitation power density [Fig. 2(c)]. The temperature

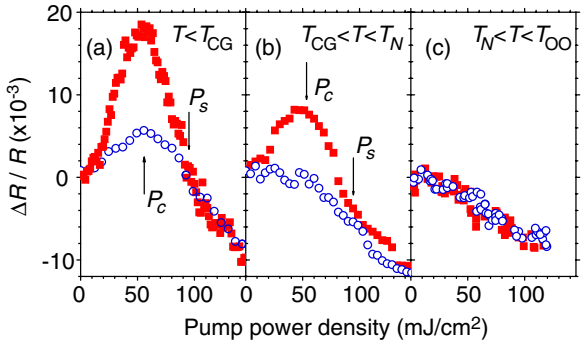

FIG. 2 (color online). Dependence of transient reflectivity on pump power density, probed at 4 ps (○) and at 100 ps (■) after optical excitation at (a) $T = 50$ K, (b) $T = 100$ K, and (c) $T = 140$ K.

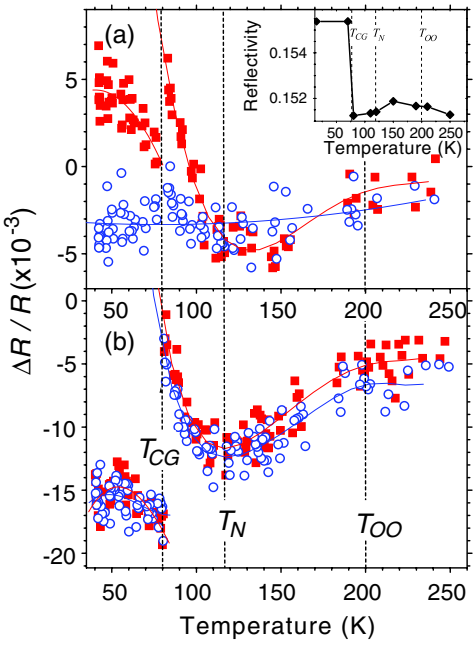

FIG. 3 (color online). Temperature dependence of transient reflectivity probed at 4 ps (○) and 100 ps (■) for excitation power densities of (a) 85 mJ/cm^2 and (b) 190 mJ/cm^2. Lines are guides for the eye. Inset shows stationary reflectance calculated using the optical constants taken from Ref. [18].

dependence of the transient reflectivity is plotted in Fig. 3 for the two excitation regimes described above: (a) $P < P_s$ and (b) $P > P_s$. In the high excitation regime anomalies are observed close to T_N for delays of both 4 and 100 ps. In the weak excitation regime the anomaly in the temperature dependence is noticeable only in the 100-ps trace, but it occurs at the same temperature as in the strong excitation regime, confirming that the background sample temperature is not affected by the optical excitation.

The disappearance of the threshold power behavior above T_N indicates that the observed photoinduced phase transition is related to the melting of the spin order. This conclusion raises the interesting question of whether the induced phase 100 ps after the optical excitation is a thermodynamically favorable (thermal) or a metastable phase. The answer to this question may be deduced from a comparison of the optically induced changes in the reflectivity at 100 ps delay (Figs. 2 and 3, solid squares) and the temperature variation of the stationary reflectivity shown in the inset of Fig. 3(a).

As temperature increases from low temperature, the reflectivity abruptly decreases at T_{CG} [inset of Fig. 3(a)]. In contrast, for $P < P_s$ the optically induced changes in reflectivity are positive [Figs. 2(a) and 3(a)]. This indicates that the spin-orbital reorientation transition does not occur even at the excitation powers, on which the spin meting takes place. Hence, for $T < T_{CG}$ the arrangements of spins and orbitals are far from thermal equilibrium even 100 ps after the optical excitation.

For higher temperature, $T > T_{CG}$, the long term (>100 ps) optically induced changes are similar to the thermally induced. Indeed, for $T_{CG} < T < T_N$ and $P < P_c$, the observed optically induced changes in reflectivity are positive [Fig. 2(b)] and resemble growth in stationary reflectivity in the same temperature range [inset of Fig. 3(a)]. At a certain temperature close to T_N both the optically induced changes in reflectivity for $P < P_c$ [Fig. 2(c)] and the slope on the temperature dependence of the stationary reflectivity [inset of Fig. 3(a)] change sign and become negative at higher temperature. This suggests that for $T > T_{CG}$ the optically excited spins and electronic subsystems reach thermal equilibrium in less than 100 ps.

Our experimental data suggest the following model. The pump pulse induces an electronic transition from the oxygen $2p$ band to the empty states in the vanadium $3d$ band [18]. Subsequently, these electrons relax to lower energy states and their excess energy excites the spin and orbital degrees of freedom. For $T > T_N$ the change in the reflectivity of YVO_3 is negative and governed by the arrangement of the occupied orbitals, which thermalizes within a time τ_1. In addition, at $T < T_N$, the photoexcited hot electrons may also transfer their energy to the ordered spin network, provoking a positive change in the reflectivity. At $P < P_c$, the subsequent thermalization of spins with the orbital degree of freedom manifests itself as the slow (τ_2) component in the transient reflectivity traces. The increased spin temperature and excited orbitals thus influence the reflectivity in opposite directions. At $P > P_c$ the power density is enough to excite the spin network above its melting point, which leads to an anomaly in the power dependency of the transient reflectivity [Figs. 2(a) and 2(b)]. However, in the range $P_c < P < P_s$, the melting of the spin order is slow and primarily governed by the thermal τ_2 equilibration with the orbital network. Finally, at $P > P_s$, the slow relaxation disappears, implying fast ($\leq \tau_1$) nonthermal spin melting. It is worth noting that the dynamics of the spin melting in YVO_3 resembles the optically induced melting of solids, where a nonthermal power threshold P_s also exists, above which the melting occurs on a picosecond time scale. Moreover, in the range $P_c < P < P_s$ the melting of solids is also slow, which has been attributed to a melt-front propagation under heterogeneous conditions [6]. This explanation, however, cannot be applied to the observed spin melting in YVO_3, because the optical excitation is homogeneous. Moreover, in YVO_3 the slow (τ_2) relaxation survives even below P_c and thus cannot be associated with a melt-front propagation.

The dynamics of the spin-orbital reordering transition is radically different. As mentioned above, at $T < T_{CG}$ the arrangement of the orbitals remains far from equilibrium even 100 ps after the optical excitation, while for $P > P_s$ melting of the spin order is triggered in less than 4 ps [Figs. 2(a) and 3(b)], confirming that the spin temperature reaches T_N (note that $T_N > T_{CG}$). This allows us to conclude that the $C \rightarrow G$ orbital transition does not occur on a picosecond time scale and that YVO_3 undergoes a transi-

tion to a metastable phase with disordered spins but *C*-ordered orbitals. We note that in our experiment the excitation power density was not sufficient to promote complete orbital melting, but nevertheless may result in partial orbital disorder.

We suggest that the striking difference between the transition dynamics of the spin-orbital reordering and the spin disordering transitions is related to the symmetry changes involved. The rapid spin melting leads to an increase in symmetry of the spin network. Conversely, the spin and orbital reordering is accompanied by a lowering of the lattice symmetry, which requires considerable time to become established across the excited volume. More generally, a symmetry rule that restricts the speed of phase transition kinetics can be formulated as follows: The transition rate from a phase with macroscopic symmetry group α to a phase with symmetry group β is limited if α is not a subgroup of β ($\alpha \not\subseteq \beta$). The limiting factor in a symmetry-breaking process is the time required to pass information about the new arrangement throughout the excited volume. For example, in YVO_3 it is limited by the propagation velocity of phonons, magnons, and/or orbital waves. This rule is in accordance with the fact that crystallization is typically slower than melting and takes several nanoseconds or longer [25]. We suggest that the symmetry rule proposed above may be valid for any kind of phase transition unless the excitation creates a coherent wave that breaks the symmetry itself. To the best of our knowledge, all reported experimental observations thus far are in agreement with this rule. Indeed, recently reported ultrafast solid-to-liquid [5–8], solid-to-solid [3,9,10], charge [11], orbital [12], and spin transitions [13] are all accompanied by $\alpha \subseteq \beta$ symmetry changes. Conversely, phase transitions that involve $\alpha \not\subseteq \beta$ symmetry changes, including the amorphous-to-crystalline transition in GeSb films [26], the paraelectric-to-ferroelectric transition in tetrathiafulvalene-*p*-chloranil [14], and the spin transition in an organometal spin-crossover material [15] have all been reported to be slow. It should be noted that even if the intermediate phase of YVO_3 is only partly *G*-type orbitally ordered as has been suggested by Miyasaka *et al.*, the corresponding transition from purely *C*-type to partly *G*-type order would require a symmetry break and, therefore, our symmetry rule restricts the dynamics of this transition as well as for the pure *C*- to *G*-type order transition.

In conclusion, we have demonstrated that the dynamics of the photoinduced homogeneous spin disordering transition in YVO_3 has a power threshold and occurs on a time scale faster than 4 ps. In contrast, the orbital reordering transition from *C*-type to *G*-type orbital order does not occur on the picosecond time scale and appears to be slower than 100 ps. We suggest that the difference in the dynamics of these phase transitions can be explained by the symmetry changes involved and we propose a symmetry rule that places a general restriction on phase transition dynamics. This rule may prove to have some useful implications; for example, the rates of certain bidirectional phase switching processes are limited, which is important to consider in designing ultrafast phase-change devices.

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*D.A.Mazurenko@rug.nl
†P.H.M.van.Loosdrecht@rug.nl

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